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SELECTION RULE EFFECTS IN ELECTRONIC EXCITATIONS OF CHEMISORBED

MOLECULES AS STUDIED BY ENERGY LOSS SPECTROSCOPY

by

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Selection rule effects associated with long-range transition dipole scattering can be significant in electron energy loss spectroscopy (ELS) for loss energies up to ~10-12 eV (or higher) on a variety of metal and semiconductor surfaces. These effects will appear in ELS studies of the electronic excitations of chemisorbed molecules; in particular, selection rule effects will suppress the intensity of certain low-lying valence transitions in several cases of current interest in chemisorption.

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ABSTRACT

Selection rule effects associated with long-range transition dipole scattering can be significant in electron energy loss spectroscopy (ELS) for loss energies up to ~10-12 eV (or higher) on a variety of metal and semiconductor surfaces. These effects will appear in ELS studies of the electronic excitations of chemisorbed molecules; in particular, selection rule effects will suppress the intensity of certain low-lying valence transitions in several cases of current interest in chemisorption.

Electron energy loss spectroscopy (ELS) provides a means to measure the characteristic vibrational and electronic excitations of chemisorbed molecules. Recent vibrational ELS studies have provided valuable new insight into the nature of chemisorbed molecules and radicals on metal surfaces and understanding of surface reactions involving these species.[1,2] Selection rule effects associated with the inelastic electron scattering process have been particularly useful in the analysis of these vibrational ELS spectra. Although there have been several studies of electronic ELS spectra for adsorbed molecules,[3-5] they have not considered selection rule effects.

The purpose of this paper is to point out that selection rule effects can play a significant role in ELS studies of the electronic excitations of adsorbed molecules on a wide variety of surfaces, including specifically some of the low-lying valence transitions of molecules of interest in chemisorption and surface reactions.

The inelastic scattering process in ELS is considered to arise mainly from long-range interaction between the fluctuating electric dipole (transition) moment of the vibrational or electronic excitation (the inelastic loss) and the charge of the primary (incident) electron.[2,6] Although questions have recently been raised as to whether short-range (non-dipole) interactions can be neglected,[7] transition dipole interactions contribute strongly to the scattering process and dominate the scattering cross-section near elastic diffraction angles.[2,6] We consider here only the transition dipole scattering.

Selection rule effects associated with inelastic long-range transition dipole scattering arise in the following way.[2,6] From classical electromagnetic theory,[8] an electric dipole fluctuation of energy E (the loss energy) associated with a surface excitation will generate a dynamic image dipole in the substrate. The magnitude of the image dipole is reduce from that of the real surface dipole by a screening factor $(\hat{\epsilon}-1)/(\hat{\epsilon}+1)$, where $\hat{\epsilon}(E)=\epsilon_1(E)+i\epsilon_2(E)$ is the complex optical dielectric function of the substrate at the loss energy E. As seen by the primary electron, the total diple moment fluctuation (the square of which determines the

scattering cross-section) is the vector sum of the real surface excitation dipole and its image in the substrate. Selection rule effects arise because real surface dipoles (a) perpendicular and (b) parallel to the surface generate image dipoles which are (a) parallel (in phase) and (b) antiparallel (180° out of phase) to the real surface dipole respectively. The time-averaged values of the total dipole moment thus reduce the cross-section for scattering by surface transition dipole components oriented parallel to the surface by a factor $|\hat{\epsilon}|^2 = \epsilon_1^2 + \epsilon_2^2$ compared to that for scattering by components oriented perpendicular to the surface. For convenience we shall refer to the factor $\epsilon_1^2 + \epsilon_2^2$ as the ELS selection rule factor or SRF.

For ELS studies of surface vibrations, energy losses are <0.4 eV and a strict selection rule usually applies. On metal surfaces, these loss energies occur in the Drude absorption region, where $|\hat{\epsilon}|$ is large and SRF$>>1$; consequently only surface vibrations with a dipole moment component normal to the surface can be observed. On semiconductor surfaces the loss energies occur in the transparent region below the band gap, but the relatively large refractive index makes SRF $(=\epsilon_1^2) >> 1$.

For electronic ELS studies of chemisorbed molecules, the region of loss energies up to ~10-12 eV is of particular interest. In this range lie the low-lying valence excitations of molecules of interest in chemisorption as well as charge transfer excitations between substrate and adsorbate orbitals. Furthermore, transition dipole excitations of oriented, chemisorbed molecules will often be polarized with respect to the surface plane (particular examples will be discussed below). This motivates our consideration of selection rule effects on various surfaces in the energy range of molecular electronic excitations.

The ELS SRF, $\epsilon_1^2 + \epsilon_2^2$, obtained from complex dielectric functions published previously, is shown over the energy range up to 25 eV in Fig. 1 for a representative sample of metal substrates, including a simple metal (Al[9]), a noble metal (Cu[10]), and several transition metals (Ta[11], Ni[12], and W[13]). Corresponding factors for three semiconductor surfaces[14] (Si, Ge, and

GaAs) are shown in Fig. 2. In the region of loss energies below 6 eV, Figs. 1 and 2 show that generally SRF $\geq$ 20., so that ELS measurements (assuming long-range dipole scattering) involve what constitutes a strong selection rule: as in the vibrational loss region, the measurements are sensitive only to surface excitations having a transition dipole moment prependicular to the surface. Above ~20 eV, SRF $\approx$ 0.5-2.0, i.e. it presents only a weak surface anisotropy factor. In the intermediate range 6-20 eV, the selection rule factor usually causes a suppression (SRF ~1-20) of the inelastic scattering cross-section for transition dipole excitations oriented parallel to the surface compared to those oriented perpendicular to the surface (although in some cases like Al and Si above 11 eV an enhancement is found, i.e. SRF < 1). Note from Figs. 1 and 2 that SRF $\gtrsim$ 4 in the range up to ~10 eV for a wide variety of solids, and in some cases (e.g. W, Cu) SRF can be $\geq$ 3 up to ~15-20 eV.[15] Consequently, a meaningful analysis of electronic ELS spectra requires consideration of the optical spectra of the substrate.

The low-lying singlet valence excitations of molecules typically lie in the range ~6-9 eV, where ELS SRF's are considerably different from unity and therefore important to consider. Table I lists these excitation energies for gas and condensed phases of several molecules of particular interest in chemisorption studies (CO[16,17], C_6H_6[18], C_2H_2[19], C_2H_4[17,20]). Table I also gives the polarization of the electric dipole (transition) moment for these excitations as derived from group theoretical considerations[21] assuming that excited and ground state symmetries on the surface are the same.

The polarization of these strong valence electronic transitions and the likely orientation of the chemisorbed molecule relative to the surface will combine to suppress the ELS intensity by significant factors for these excitations in many interesting cases. For example, the CO molecule is normally bonded to transition metal surfaces with its axis normal to the surface,[22,23] so that the transition dipole of the $5\sigma \rightarrow 2\pi^*$ first singlet valence excitation is parallel to the surface. For the unsaturated hydrocarbons C_6H_6, C_2H_2, and C_2H_4 on trans-

ition metals, π-bonded and di-σ-bonded (rehybridized) chemisorption species[24] are believed to lie with the C-C bond axes parallel to the surface,[1,24] so that $\pi \to \pi^*$ transitions are also polarized parallel to the surface. Because the CO $5\sigma \to 2\pi^*$ and hydrocarbon $\pi \to \pi^*$ valence excitations are polarized parallel to the surface for likely chemisorption bonding geometries on transition metal surfaces, their intensity will be suppressed considerably in the ELS spectra.

These selection rule considerations may have specific application in the interpretation of the ELS spectrum of CO chemisorbed on transition and noble metal surfaces.[3,4,25] In these cases, two characteristic losses are seen, one at ~4.5-6.0 eV and another at ~13-14 eV. By analogy with transition metal carbonyl spectra, the former has been attributed[3] to charge transfer excitations from the metal to the empty CO ($2\pi^*$) orbital. This assignment is reasonable since (i) charge transfer excitations will always have a transition dipole moment *component perpendicular to the surface* (and possibly a component parallel to the surface) and (ii) charge transfer transitions in the spectra of organometallics are generally strong. However, the interpretation of the remainder of the spectrum[3] is questionable in view of selection rule effects.

The optical[17] and FLS[16] spectra of molecular CO consist of a peak at ~8.0-8.4 eV, another near 13-14 eV which is ~3-4× as strong as the first, and a weak shoulder near 11 eV. The loss peak at 13-14 eV for chemisorbed CO appears to be associated with corresponding structure in the spectrum of molecular CO.[16] Because no structure has been observed near 8-10 eV in the ELS spectrum of the chemisorbed molecule, it has been suggested[3] that the first singlet valence excitation ($5\sigma \to 2\pi^*$ in one-electron terminology) is shifted up (by ~5 eV) from its position at ~8.0-8.4 eV in the gas or solid phase to ~13-14 eV in the chemisorbed phase due to ground state chemisorption bonding effects. The validity of such an interpretation is questionable because: (i) the intensity of the first singlet transition would be suppressed by a SRF ~3-6× if it lies at 10 eV or below when the molecule is chemisorbed; (ii)

this transition is already considerably weaker than the structure near 13-14 eV in the spectrum of molecular CO; and (iii) the strong charge transfer band near 4.5-6.0 eV may partly mask the singlet valence excitation if the latter lies at ~8 eV or below for the chemisorbed molecule. Thus it is not clear whether the ELS measurements can provide a reliable estimate of the first singlet valence excitation energy for CO chemisorbed on transition or noble metal surfaces.

In conclusion, the interpretation of the electronic ELS spectra of chemisorbed molecules should be made in light of selection rule effects as outlined above. Likely orientations of the chemisorbed molecule with respect to the surface can be inferred from angle-resolved[22] (or sometimes angle-integrated[24]) ultraviolet photoemission studies, vibrational ELS measurements[1,2] (where strict selection rules apply), or low energy electron diffraction analysis. It is important that further attention be given to the detailed microscopic scattering mechanisms and the contribution of long-range dipole scattering in ELS spectra.

References

1. H. Ibach, Applic. of Surface Science $\underline{1}$, 1 (1977).

2. H. Froitzheim, in <u>Electronic Spectroscopy for Surface Analysis</u>, ed. by H. Ibach (Springer, N.Y., 1977).

3. F. P. Netzer, R. A. Wille, and J. A. D. Matthew, Solid State Commun. $\underline{21}$, 97 (1977).

4. J. Küppers, Surface Science $\underline{36}$, 53 (1973); K. Christmann, O. Schober, and G. Ertl, J. Chem. Phys. $\underline{60}$, 4719 (1974); H. Papp and J. Pritchard, Surface Science $\underline{53}$, 371 (1975); G. McElhiney, H. Papp, and J. Pritchard, Surface Science $\underline{54}$, 617 (1976).

5. M. Nishijima and K. Fujiwara, Solid State Commun. $\underline{24}$, 101 (1977); K. Fujiwara, H. Ogata, and M. Nishijima, Solid State Commun. $\underline{21}$, 895 (1977).

6. E. Evans and D. L. Mills, Phys. Rev. B $\underline{5}$, 4126 (1972); D. L. Mills, Surface Science $\underline{48}$, 59 (1975).

7. W. Ho, J. W. Davenport, and J. R. Schrieffer, to be published in J. Vac. Sci. Technol., March/April, 1978.

8. J. D. Jackson, <u>Classical Electrodynamics</u> (Wiley, N. Y., 1962), p. 110.

9. H. Ehrenreich, H. R. Phillip, and B. Segall, Phys. Rev. $\underline{132}$, 1918 (1963).

10. H. Ehrenreich and H. R. Philipp, Phys. Rev. $\underline{128}$, 1622 (1962).

11. J. H. Weaver, D. W. Lynch, and C. G. Olson, Phys. Rev. B $\underline{10}$, 501 (1974).

12. R. C. Vehse and E. T. Arakawa, Phys. Rev. $\underline{180}$, 695 (1969); T. J. Morawec, J. C. Rife, and R. N. Dexter, Phys. Rev. B $\underline{13}$, 3297 (1976).

13. J. H. Weaver, C. G. Olson, and D. W. Lynch, Phys. Rev. B $\underline{12}$, 1293 (1975).

14. H. R. Philipp and H. Ehrenreich, Phys. Rev. $\underline{129}$, 1550 (1963).

15. Dielectric screening by the substrate also acts to suppress the intensity of transition dipole excitations polarized parallel to the surface as seen in surface reflectance spectroscopy (e.g., see J. Anderson, G. W. Rubloff, M. A. Passler, and P. J. Stiles, Phys. Rev. B $\underline{10}$, 2401 (1974), references therein, and Ref. 25 of this paper). Contrary to the case of ELS, however, transitions polarized perpendicular to the surface can

be eliminated from the reflectance measurements by using s-polarized light to make those parallel to the surface more easily observed.

16. H. J. Hinz, Vacuum Ultraviolet Radiation Physics, ed by E. E. Koch et al (Pergamon, New York, 1975), p. 176.

17. A. Rauk and J. M. Barriel, Chem. Phys. $\underline{25}$, 409 (1977).

18. E. E. Koch and A. Otto, Int. J. Radiat. Phys. Chem. $\underline{8}$, 113 (1976); U. Killat, J. Phys. C:Solid State Phys., $\underline{7}$, 2396 (1974); M. Shiho, Japan. J. Appl. Phys. $\underline{12}$, 314 (1973).

19. D. F. Dance and I. C. Walker, J. Chem. Soc. Faraday Trans. II $\underline{70}$, 1426 (1974).

20. R. J. Buenker and S. D. Peyerimhoff, Chem. Physics $\underline{9}$, 75 (1976): A. J. Merer and R. S. Mulliken, Chem. Rev. $\underline{69}$, 639 (1969); M. B. Robin, Higher Excited States of Polyatomic Molecules, Vol. 2 (Academic Press, N. Y., 1975).

21. M. Tinkham, Group Theory and Quantum Mechanics (McGraw-Hill, N.Y., 1964); J. N. Murrell, The Theory of the Electronic Spectra of Organic Molecules (Wiley, N.Y., 1963); H. Suzuki, Electronic Absorption Spectra and Geometry of Organic Molecules (Academic, N.Y. 1967).

22. C. L. Allyn, T. Gustafsson, and E. W. Plummer, Chem. Phys. Letters $\underline{47}$, 127 (1977); G. Apai, P. S. Wehner, R. S. Williams, J. Stöhr, and D. A. Shirley, Phys. Rev. Letters $\underline{37}$, 1497 (1976); R. J. Smith, J. Anderson, and G. J. Lapeyre, Phys. Rev. Letters $\underline{37}$, 1081 (1976).

23. T. N. Rhodin, J. Kanski, and C. Brucker, Solid State Commun. $\underline{23}$, 723 (1977).

24. J. E. Demuth and D. E. Eastman, Phys. Rev. Letters $\underline{32}$, 1123 (1974); Phys. Rev. B $\underline{13}$, 1523 (1976); C. Brucker and T. Rhodin, J. of Catalysis $\underline{47}$, 214 (1977); J. E. Demuth, Chem. Phys. Letters $\underline{45}$, 12 (1977).

25. G. W. Rubloff and J. L. Freeouf, to be published.

Table I. Energy and polarization, and assignment of strong valence electronic transitions in CO, C_6H_6, C_2H_4, and C_2H_2.

Molecule	Transition Energy (eV)	Assignment	Polarization
CO	~8.0-8.4[a]	$5\sigma - 2\pi^*$ $(X^1\Sigma^+ \rightarrow A^1\Pi)$	Normal to C≡O axis
C_6H_6	~6.9[b] (gas) ~6.4[b] (solid) }	$\pi \rightarrow \pi^*$ $(^1A_{1g} \rightarrow {}^1E_{1u})$	In molecular plane
C_2H_2	~7.3[c]	$\pi \rightarrow \pi^*$ $(^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+)$	Along C≡C axis
C_2H_4	~7.7[d]	$\pi \rightarrow \pi^*$	Along C=C axis

[a]Refs. 16, 17.

[b]Ref. 18.
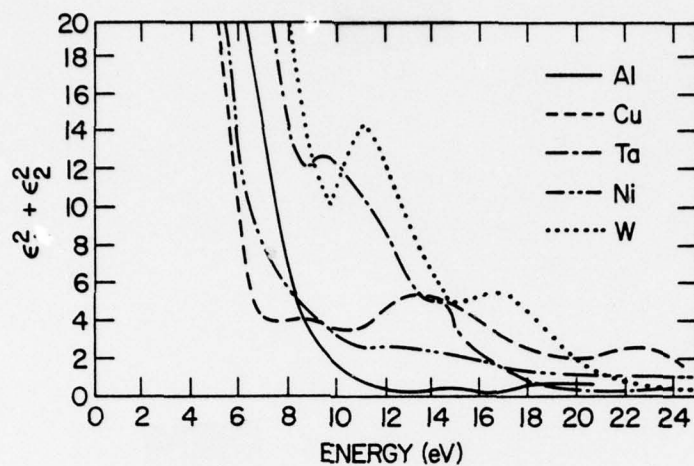
[c]Ref. 19.

[d]Refs. 17, 20.

Fig. 1.   Spectral dependence of ELS selection rule factors $\epsilon_1^2 + \epsilon_2^2$ for a variety of metal surfaces, as calculated from complex dielectric functions for Al (Ref. 9), Cu (Ref. 10), Ta (Ref. 11), Ni (Ref. 12), and W (Ref. 13).
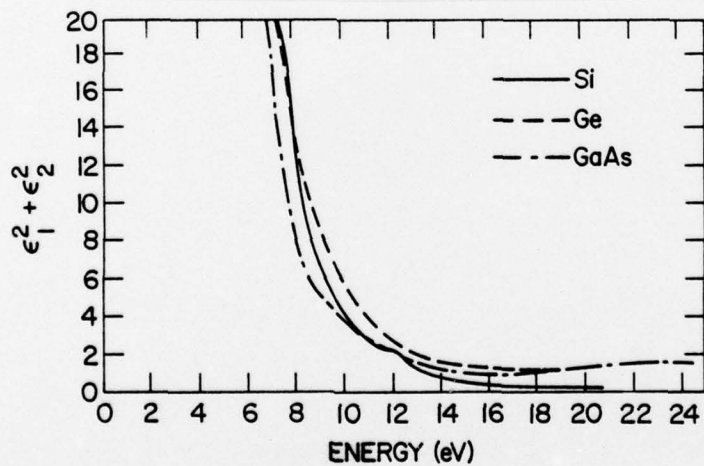

Fig. 2.   Spectral dependence of ELS selection rule factors $\epsilon_1^2 + \epsilon_2^2$ for several semi-conductor surfaces (Ref. 14), Si, Ge, and GaAs.
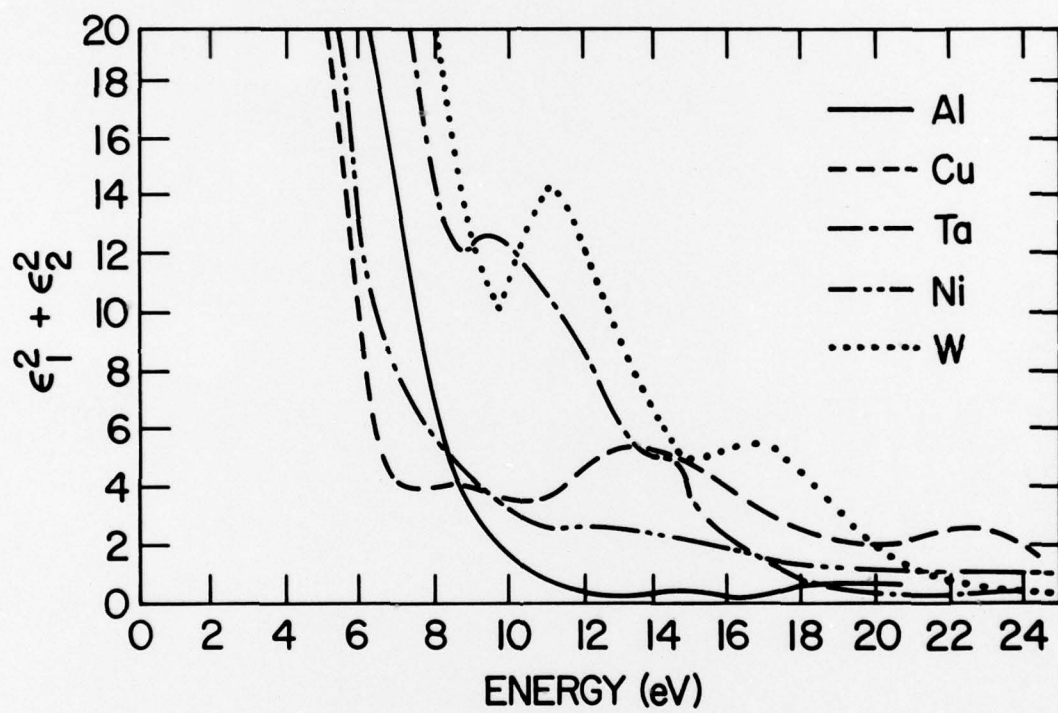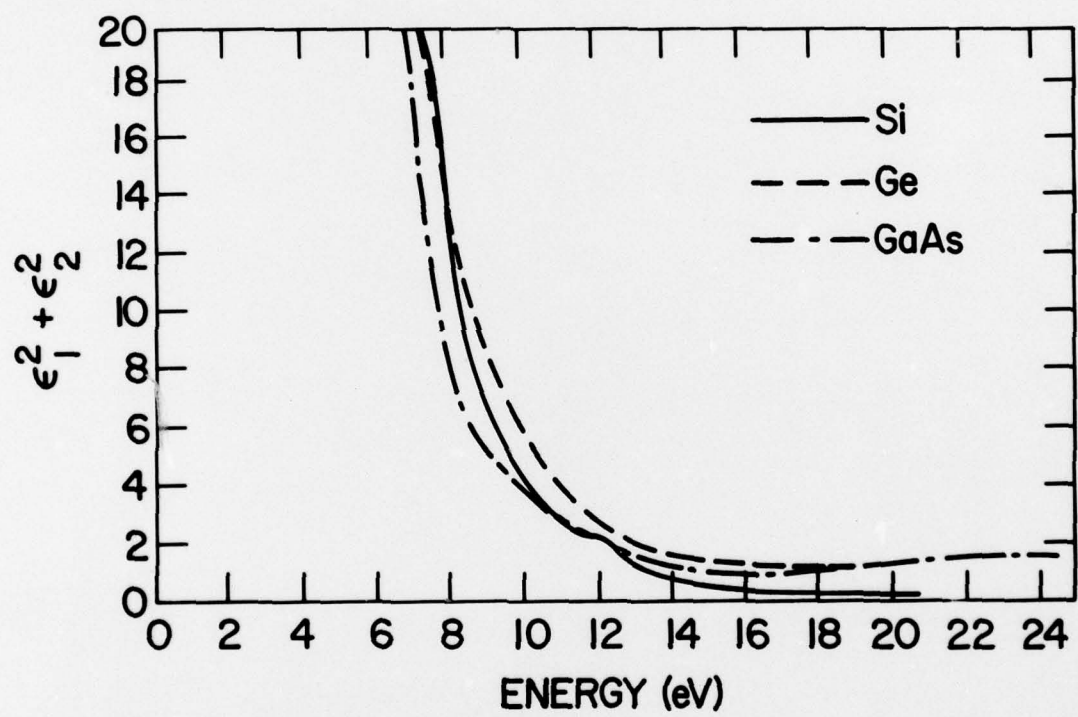
Fig. 1

Fig. 2